A New Titration Method for the Exact Determination of Phosphorus

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DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in the Faculty of Pure Science,
Columbia University.

BY

GROVER C. CHANDLEE, Ph.B., M.S., M.A.

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A NEW TITRATION METHOD FOR THE EXACT DETERMINATION OF PHOSPHORUS

In the usual acidimetric titration method for the determination of phorphorus which depends upon the precipitation of the yellow ammonium phosphomolybdate, its solution in an excess of standard alkali and titration of the excess with standard acid, the results have always been attended by considerable uncertainty as to their accuracy. This uncertainty arises through lack of knowledge of the complex ammonium phosphomolybdate both as to composition and properties, as well as of other factors connected with the technic of the determination. Among these may be mentioned, the co-precipitation of molybdic acid or its adsorption upon the yellow phosphomolybdate precipitate, the influence of ammonia upon the titration and the choice of the proper indicator to give the correct end point of the titration.

A review of the literature shows that while variations of the method have been made over a wide range of conditions, investigators are still dissatisfied with this method as one of precision.

E. Thilo (Chem. Ztg. 11, 193, (1887), precipitated at 70° C with a molybdate solution containing one part of molybdic acid, three parts of ammonium nitrate and fifteen parts of nitric acid. He allowed the solution to stand five minutes, filtered, washed with twenty percent ammonium nitrate solution, dissolved the precipitate in ammonium hydroxide and titrated back with sulphuric acid using litmus as an indicator.

F. Hundeshagen (Z. f. Anal. Chem. 28, 141, (1889), dissolved the yellow precipitate in excess standard sodium hydroxide and titrated back with nitric acid using phenolphthalein as the indicator. In his analytical studies of ammonium phosphomolybdate he found its composition under all conditions, when free from molybdic acid and other impurities, to be $(NH_4)_3PO_4$, 12 MoO_3, and that one molecule required for neutralization 23 molecules of alkali.

C. E. Manby (J. Anal. and Appl. Chem. 6, 82, (1892), precipitated near boiling, dissolved the yellow precipitate in fifteen percent ammonium hydroxide, acidified with nitric acid, and evaporated to dryness and heated gently to expel nitric acid and ammonium nitrate. He then titrated using the same solutions and indicator that Hundeshagen employed.

J. O. Handy (J. Anal. and Appl. Chem. 6, 204, (1892), precipitated at 85° C, avoided the evaporation and heating and titrated directly as Thilo and Hundeshagen did, using standard soda and phenolphthalein.

M. Rothberg and W. A. Auchinvole (J. Anal. and Appl. Chem. 6, 243, 1892), precipitated at 40° C, washed the precipitate five times with one percent nitric acid, five times with 0.3 percent potassium nitrate, titrated with sodium hydroxide and back with nitric acid.

H. Pemberton, Jr., (J. A. C. S., 15, 382, (1893), 16, 278, (1894), made an extended investigation of this method. He precipitated at boiling temperature with aqueous ammonium molybdate, washed the precipitate with water, titrated with potassium hydroxide free from carbonate and back with hydrochloric acid. In his first work he found one molecule of ammonium phosphomolybdate required 23.2 molecules of alkali, but in his later work he obtained the ration 23 to 1.

B. W. Kilgore (J. A. C. S., 16, 765, (1894), 17, 950, (1895), investigated Pemberton's method and found that it gave results that were slightly high, due, he believed, to the presence of molybdic acid or an ammonium molybdate in the precipitate. He modified the method in that he precipitated at 60° C instead of at boiling temperature as Pemberton did and used a molybdate reagent containing nitric acid. Kilgore washed the precipitate with dilute nitric acid, then with 3 percent potassium or ammonium nitrate and finally with water until no longer acid. He dissolved the precipitate in standard potassium hydroxide solution and titrated back with nitric acid using phenolphthalein as the indicator.

G. H. G. Lagers (Z. f. Anal. Chem. 47, 561, (1908), found the formula for the ammonium phosphomolybdate precipitate to be $(NH_4)_3PO_4$, 12.65 MoO_3 which requires 24.30 molecules of sodium hydroxide for neutralization.

Many other authors have investigated the effect of the temperature of precipitation upon the composition of the ammonium phosphomolybdate precipitate. Wood (J. Anal. Chem. 1, 138, (1887), precipitated at 30-40° C. Meineke (Chem. Ztg. 20, 108, (1896), at 50-60°, Gladding (J. A. C. S. 18, 23, (1896), at 50°, Woy (Chem. Ztg. 21, 441, (1897), at boiling temperature, Jorgensen (Z. f. Anal. Chem. 46, 370, (1907), at 50°, Chesneau (Compt Rend. 146, 758, (1908), at 65-70°, Artmann and Brandis (Z. f. Anal. Chem. 49, 1, (1910), at 40-50°, and Hibbard (J. Ind. and Eng. Chem. 5, 998, (1913), at 65°.

N. E. Johann (Dissertation, Columbia University, 1921), obtained a precipitate of constant composition by precipitating in a cold solution, using a precipitating reagent prepared by mixing the ammonium molybdate solution and the nitric acid solution in the proper proportion just before using.

Various attempts have been made to overcome some of the difficulties encountered in titrating the yellow precipitate, par-

ticularly as regards difficulties due to the presence of ammonia in the molecule. High results are believed to be due in part to displacement of ammonia by the fixed alkali used in titration and to interference by ammonia with the end point when phenolphthalein is used as the indicator.

A. Neumann (Z. Physiol. Chem. 37, 129, (1903), dissolved the precipitate in excess sodium hydroxide solution, boiled until free from ammonia and titrated back with sulphuric acid using phenolphthalein as the indicator. One molecule of phosphorus pentoxide was equivalent to 56 molecules of sodium hydroxide. Neumann believes the formula for the yellow precipitate to be $(NH_4)_3PO_4$, 12 MoO_3, 2 HNO_3.

J. P. Gregersen (Z. Physiol. Chem. 53, 453, (1907), studied Neumann's method and suggests in the final titration to add a slight excess of standard acid, boil to drive out the carbon dioxide and then titrate back with sodium hydroxide.

P. L. Hibbard (J. Ind. and Eng. Chem. 5, 998, (1913), tried to improve the end point by removing phosphoric acid by means of neutral barium chloride.

W. Heubner (Biochem. Zeit. 64, 393, (1914), in applying Neumann's method obtained better results when he used 1 cc of N/2 sodium hydroxide equal to 0.565 mg. of phosphorus instead of 0.553 the theoretical value.

S. L. Jodidi (J. A. C. S. 37, 1708, (1915), also found Neumann's factor too low.

K. G. Falk and K. Sugiura (J. A. C. S. 37, 1507, (1915), in their investigation of Neumann's method of precipitating phosphorus as ammonium phosphomolybdate in the presence of sulphuric acid found that the precipitate thus formed did not contain nitric acid, as shown by the fact that the titration values were the same whether or not the precipitate was dried at 120°. They found, however, that the precipitate formed under the conditions studied contained sulphate and additional molybdic acid as an essential part of the molecule and had the formula 4 $(NH_4)_3PO_4$, 12 MoO_3 + $(NH_4)_2SO_4$, 5 MoO_3. They removed the ammonia before titration either by boiling or by adding formaldehyde.

N. E. Johann (Dissertation, Columbia University, 1921), showed that the presence of sulphuric acid or hydrochloric acid had no effect on the precipitation of phosphorus as ammonium phosphomolybdate and that neither sulphate nor chloride was contained in the molecule when the method was carried out under the conditions which she prescribed.

H. Kleinmann (Biochem. Zeit. 99, 19, (1919), obtained low results by Neumann's method when the theoretical factor was used. He recommends also washing the precipitate with 50 percent alcohol instead of water.

It is apparent that investigators differ widely regarding many of the fundamental points of the method for the determination of phosphorus by precipitation as ammonium phosphomolybdate and subsequent titration with standard alkali and acid. Temperatures for precipitation ranging from room temperature to boiling temperature have been suggested, with the view of avoiding molybdic acid in the precipitate and obtaining a precipitate of constant composition. The influence of ammonia upon the titration has brought many modifications in the procedure, none of which seem to be wholly satisfactory. Difficulties are encountered in technic in boiling out either ammonia or carbon dioxide before titration as suggested by Neumann and Gregersen and in the evaporation to dryness followed by heating to expel ammonium nitrate and nitric acid according to the method of Manby. Variation in the method of washing the precipitate in preparation for titration includes a wide range of substances. That much uncertainty exists regarding the composition of the yellow precipitate is evidenced by the fact that different investigators find nitric acid, sulphuric acid and hydrochloric acid as an essential part of the molecule. Wide variation is encountered also in the statements of the authors as to the number of moles of alkali equivalent to one mole of the phosphomolybdate precipitate. The values appearing most frequently are 23, 24.3, and 26 moles of alkali per mole of phosphomolybdate precipitate. Removal of ammonia by boiling with excess of alkali before the back titration with standard acid does not seem to bring any better agreement regarding the factor to be used. Neumann found that one mole of the precipitate required 28 moles of alkali but Heubner, Jodidi and Kleinmann all found Neumann's factor too low.

The use of a fixed alkali salt of phosphomolybdic acid naturally suggests itself as a possibility in avoiding difficulties met with in titrating the ammonium salt. Lithium and sodium do not yield a precipitate with phosphomolybdic acid. Potassium phosphomolybdate has been studied with a view to its use both for the estimation of phosphorus and for the qualitative and quantitative determination of potassium.

O. Korschelt (Chem. Centrl. Blatt, 8, 487, (1877), describes a method for the estimation of phosphorus in iron and iron oxide by precipitation as potassium phosphomolybdate. He prepared

a reagent in the following manner. One part of molybdic acid was dissolved in 1 part of pure potassium hydroxide and 6 parts of water. A solution of ½ part of tartaric acid in 2 parts of water was added and then 7½ parts of nitric acid. This solution was heated to boiling and filtered hot. About enough sample was taken so that the resulting potassium phosphomolybdate weighed 0.5 to 0.75 gram. The sample was dissolved in hot nitric acid, the volume being kept under 50 cc. Precipitation was effected by filtering the solution into the potassium molybdate reagent heated on a water bath. The precipitate was washed with water containing nitric acid, then with alcohol, dried at 120-130° C for twenty minutes and weighed.

A. Schlicht (Chem. Ztg. 30, 1299, (1906), 32, 1125, (1908), and A. Grete (Chem. Ztg. 33, 1128, (1909), describe reagents for the estimation of potassium as potassium phosphomolybdate.

R. Finkener (Ber. 11, 1638, (1878), studied Korschelt's method for the precipitation of phosphorus as potassium phosphomolybdate at high temperature and in the presence of tartaric acid and found that in an iron containing 0.1 percent phosphorus the presence of phosphorus might not even be detected.

Results obtained in this investigation by precipitating phosphorus as potassium phosphomolybdate coincide in the main with those obtained by Finkener. With a low phosphorus iron, requiring a large sample, it is practically impossible to keep the volume of solution within the prescribed limit. Furthermore when the temperature is raised sufficiently high to insure complete precipitation of phosphorus, molybdic acid is almost invariably present in the precipitate. Satisfactory results were obtained when the phosphorus content was 0.007 grams per 100 cc of solution or above and the determination was completed by reprecipitating the phosphorus as magnesium ammonium phosphate. Because of the difficulty of obtaining, at the high temperature required, a precipitate free of molybdic acid, precipitation as potassium phosphomolybdate was found unsatisfactory for the volumetric method.

A search of the literature failed to show the exact solubilities of the phosphomolybdates of the alkali metals. Their relative solubility may be indicated by adding an equivalent quantity of a salt of each to equal volumes of solutions of varying concentration of phosphomolybdic acid and noting the point at which a precipitate fails to form. By this method a solubility in an inverse order to their atomic weights was indicated. Cesium phosphomolybdate is, therefore, from the standpoint of solubility, the

most promising and was chosen for study as to its suitability for the acidimetric method.

The low solubility indicated gave promise also of complete precipitation of phosphorus as cesium phosphomolybdate in cold solution, a condition N. E. Johann obtained with ammonium phosphomolybdate, with certain limitations. Undoubtedly a good deal of the difficulty chemists have had in obtaining a precipitate of constant composition is due to the varying conditions of precipitation.

The literature does not show a very comprehensive study of the compounds of cesium with molybdic acid and with phosphomolybdic acid. Only a few investigations are recorded and there is little agreement regarding the composition and properties of the compounds described.

A. Rosenheim (Z. Anorg. Chem. 15, 180, (1897), prepared cesium paramolybdate, 3 Cs_2O, 7 MoO_3 x H_2O, by treating a solution containing one mole of cesium carbonate with two moles of molybdic acid. He states that the salt is only slightly soluble and crystallizes from a dilute solution.

C. Wempe (Z. Anorg. Chem. 78, 298, (1912), prepared the same salt by letting evaporate slowly a solution of cesium carbonate saturated with molybdic acid. He found the salt easily soluble in water which contradicts Rosenheim's statement. Wempe describes other cesium molybdates having the formulae: Cs_2O, 4 MoO_3, 3 H_2O and 5 Cs_2O, 12 MoO_3, 11 H_2O.

W. Muthmann and W. Nagel (Ber. 31, 1836, (1898) obtained, by fusing one mole of cesium carbonate with three moles of molybdic acid, a melt which on extracting with water left as insoluble residue Cs_2O, 4 MoO_3. By evaporating the solution they obtained a hydrate having the formula Cs_2O, 4 MoO_3, 2 H_2O.

F. Ephraim and H. Herschfinkel (Z. Anorg. Chem. 64, 263, (1909), on heating a solution containing one mole of cesium hydroxide and two moles of molybdic acid obtained a slightly soluble molybdate, rich in molybdic acid. The mother liquor by evaporation gave a cesium holybdate having the formula 2 Cs_2O, 5 MoO_3, 5 H_2O,—not paramolybdate. By evaporating the solution with varying quantities of nitric acid they obtained cesium molybdates having the formulae: Cs_2O, 5 MoO_3, 3 H_2O: Cs_2O, 3 MoO_3, H_2O and Cs_2O, 16 MoO_3, 8 H_2O.

These authors (Z. Anorg. Chem. 65, 237, (1910), also investigated the phosphomolybdates of cesium and prepared a yellow salt having the formula 2 Cs_2O, P_2O_5, 14 MoO_3, 3 H_2O, by adding phosphoric acid and nitric acid to a solution of cesium molybdate. They obtained a white salt of the formula 3 Cs_2O, P_2O_5, 6 MoO_3, 8 H_2O, by adding one-half mole of phosphoric

acid and then one mole of molybdic acid to a solution containing one mole of cesium carbonate and heating.

From the foregoing it would appear that much uncertainty exists regarding the composition of the molybdates and phosphomolybdates of cesium, particularly regarding those formed in hot solution. With regard to some of the substances described there seems to be reason for doubt whether they are chemical individuals or isomorphous mixtures. However in spite of the lack of knowledge regarding these substances it seemed worth while, because of the low solubility indicated, to see if a precipitate of definite composition could not be obtained.

PREPARATION OF MATERIALS

Potassium dihydrogen phosphate.

Potassium dihydrogen phosphate was chosen as a standard substance for obtaining a known weight of phosphorus. This salt can easily be recrystallized, it contains no water of hydration and it can be dried to constant weight giving a definite compound of the formula KH_2PO_4. Its purity can be tested by igniting a known weight to metaphosphate. A good grade of the salt was recrystallized several times and dried at 110° C. A test of its purity by igniting portions of known weight to the metaphosphate resulted as follows:

Weight of KH_2PO_4 Taken	Weight of KPO_3 Calculated	Weight of KPO_3 Found	Difference
3.0973 g	2.6875 g	2.6873 g	—.0002 g
3.2904	2.8551	2.8552	+.0001
3.9258	3.4064	3.4060	—.0004
3.6718	3.1860	3.1855	—.0005

Preparation of a standard solution of potassium dihydrogen phosphate.

In titration methods for the determination of phosphorus a smaller quantity of potassium dihydrogen phosphate than can be weighed accurately is wanted, consequently a solution was prepared and standardized in the following manner.

1.5 grams of potassium dihydrogen phosphate, purified as described above, were dissolved in water and the solution made up to a volume of 2000 cc. After thorough shaking and standing for several hours portions of from 20 cc to 50 cc were measured from a calibrated burette into weighed platinum dishes, evaporated to dryness and the phosphate ignited to metaphosphate. Portions for analysis were measured either from calibrated burettes or pipettes. The solution was restandardized at frequent

intervals. A typical set of results obtained in standardization follows:

cc of Solution Taken	Weight of KPO_3 Found	Weight of Phosphorus Calculated
20	0.0125 g	0.00328 g
20	0.0125	0.00328
20	0.0125	0.00328
20	0.0126	0.00330

Molybdate precipitating reagent.

A solution of cesium molybdate was prepared by dissolving 82 grams of cesium hydroxide in 250 cc of water and adding 37 grams of molybdic acid free from ammonia. The solution was heated to 85° C and filtered. A second solution was prepared by adding 500 cc of concentrated nitric acid to 500 cc of water. The precipitating reagent was prepared by adding solution 1 to solution II in the proportion of 15 cc of the former to 30 cc of the latter, heating at 80-85° C for an hour, allowing to cool and filtering. The solution thus prepared remains clear after standing several weeks.

Washing solutions.

(A) The solution found most satisfactory for the first washing of the yellow phosphomolybdate precipitate contained 25 cc of concentrated nitric acid per litre of solution.

(B) To wash the yellow precipitate free from acid for titration, 95 percent alcohol (distilled over sodium hydroxide) saturated with potassium nitrate was used.

Preparation of standard solutions of acid and alkali.

Sodium hydroxide solution.—Solid sodium hydroxide, purified by alcohol, was placed in a glass stoppered cylinder and distilled water in insufficient quantity to dissolve the material was added. After standing twenty-four hours a quantity of the clear solution was removed and diluted to make a solution approximately tenth normal.

Nitric acid solution.—Nitric acid, specific gravity 1.40, free from impurities, was added to water to make a solution approximately tenth normal.

The nitric acid solution was standardized by titration against Baker's analyzed sodium carbonate which had been dried at 110° C for twenty-four hours. The sodium hydroxide solution was standardized by titrating a measured quantity with the standard nitric acid, using phenolphthalein as the indicator. The factor

obtained for the nitric acid solution was .1057 and for the sodium hydroxide solution .1073. This standardization was checked with Bureau of Standards benzoic acid. The solutions were re-standardized at frequent intervals.

DETERMINATION OF THE RATIO OF SODIUM HYDROXIDE TO PHOSPHORUS

The cesium molybdate reagent, prepared as indicated, is sufficiently sensitive to low concentrations of phosphate ion to admit of precipitation in cold solution, even in the presence of ferric ion as will be shown later. The time required for complete precipitation of phosphorus as cesium phosphomolybdate is influenced by the hydrogen ion concentration. A high concentration of hydrogen ion retards the formation of the precipitate appreciably and ultimately would prevent complete precipitation of the phosphorus. The hydrogen ion concentration must be high enough to prevent formation of a precipitate when the reagent is diluted by adding it to a solution for the precipitation of phosphorus. By blank tests it was found that no precipitate resulted in twenty-four hours when 45 cc of the reagent had been added to 100 cc of water. In the results recorded in this investigation the volume of the phosphate solution was kept at 100 cc.

When the phosphorus content is 1.0 mg. or above precipitation begins immediately. In case of lesser amounts the precipitate forms after stirring for a short time. The precipitate settles somewhat slowly. It was found that filtering could best be carried out by first stirring paper pulp in the solution to absorb most of the precipitate and then filtering by suction, using a platinum cone, through a hard filter paper to which paper pulp had been added.

Method of procedure.

A quantity of the standard phosphate solution was measured from a calibrated burette into enough water to make the volume 100 cc. 5.0 grams of cesium nitrate were added and to the cold solution were added rapidly 45 cc of the molybdate reagent. After stirring, the solution was allowed to stand from twelve to eighteen hours. The solution was filtered in the manner indicated and the precipitate washed with the nitric acid solution until 1 or 2 cc of the wash water showed no test for molybdenum upon addition of a drop or two of ammonium sulphide. The precipitate was then washed with the alcohol solution until free from acid. The filter paper containing the precipitate was transferred to the original beaker, an excess of standard sodium hydroxide,

free of carbonate, added and the excess titrated with nitric acid using phenolphthalein as the indicator.

Proceeding in this manner the ratio of phosphorus taken to sodium hydroxide used in the titration of cesium phosphomolybdate was determined as follows:

P Calculated From KH_2PO_4 Taken	cc N/10 NaOH Used	Factor (gr. P. Per cc of N/10 NaOH
.00328 g	23.81	.000137
.00328	23.76	.000138
.00328	23.71	.000138
.00328	24.08	.000136
.00328	24.05	.000136
.00328	23.94	.000137
.00328	23.71	.000138
.00328	24.03	.000136
.00328	24.21	.000135
.00328	24.15	.000135
.00328	24.10	.000136
.00328	24.17	.000135
Average	23.98	.000136
	Average Deviation	.0000009
		(6.6 parts per 1000)

Assuming the composition of the yellow phosphomolybdate to be $(NH_4)_3PO_4$, 12 MoO_3 so far as its active constituents in a neutralization process are concerned, reaction with NaOH may be represented by the equation.

$(NH_4)_3PO_4$, 12 MoO_3 + 23 $OH^- \rightarrow HPO_4^=$ + 12 $MoO_4^=$ + 11 H_2O, which gives a ratio of P:NaOH = 1:23. Calculating the ratio for the cesium phosphomolybdate, using the average given above, the following result is obtained:

P Taken Grams	P Gram Atoms	NaOH cc N/10	NaOH Moles
.00328	.0001056	23.98	.002398
P: NaOH = .0001056: .002398			
1 : 22.7			

In order to determine the reliability of the factor obtained in the previous work for the determination of phosphorus, a quantity of the standard dihydrogen phosphate solution that would give an amount of phosphorus about equivalent to that found in steel was taken and the phosphorus precipitated and the deter-

mination completed in the manner outlined, with the following results:

P Calculated From KH_2PO_4 Taken	P Calculated From Titration Data	Difference
.00120	.00118	—.00002
.00120	.00117	—.00003
.00120	.00119	—.00001
.00120	.00118	—.00002
.00120	.00116	—.00004
.00017	.00017	.00000
.00017	.00019	+.00002
.00017	.00017	.00000
.00017	.00016	—.00001

An attempt was made to compare results obtained by the cesium method with results obtained by precipitation of phosphorus as ammonium phosphomolybdate but was given up for the reason that in every titration of the yellow ammonium phosphomolybdate precipitate the odor of ammonia was distinctly noticeable. Also due to hydrolysis during washing it was impossible to obtain the precipitate in a neutral condition for titration.

INTERFERENCE OF ARSENIC

Sonnenschein (J. Prakt. Chem. 53, 343, (1851), investigated the action of ammonium molybdate with arsenic acid and found that while at high temperatures (100°) a yellow precipitate resulted, with properties quite similar to the yellow phosphomolybdate, at ordinary temperatures no precipitate was formed

While this is satisfactory as far as the action of ammonium molybdate with arsenate ion alone is concerned, it gives no indication of its behavior with arsenate ion in the presence of an appreciable quantity of phosphate ion.

M. Frank and F. W. Hinrichsen (Stahl u, Eisen, 28, 295, (1908), investigated the effect of small quantities of arsenic on the results obtained in the determination of phosphorus in steels when precipitated as ammonium phosphomolybdate. They found that in the presence in steel of arsenic up to 0.05 percent, a variation of 0.015 percent phosphorus must be allowed when the analysis is made without removing the arsenic. In their investigation the phosphomolybdate was precipitated at room temperature.

The cesium molybdate reagent used in this work will precipitate arsenic, when present as the arsenate ion, from cold solution. Yellow precipitates obtained in the precipitation of phosphorus in iron and steel gave positive tests for arsenic both by the Marsh test and by the Sanger-Black test. It is essential

therefore that arsenate ion be absent from a solution in which phosphorus is to be precipitated by this reagent. Results obtained in this work would indicate that the precipitation of arsenic is quantitative, but this has not yet been fully investigated.

F. Ephraim and H. Herschfinkel (Z. Anorg. Chem 65, 237, (1910), describe a yellow cesium arsenomolybdate having the formula 4 Cs_2O, As_2O_5, 26 MoO_3, 15 H_2O, obtained by adding nitric acid and arsenic acid to a solution of a cesium molybdate and warming to about 50° C.

THE DETERMINATION OF PHOSPHORUS IN IRON AND STEEL

The determination of phosphorus in iron and steel presents some difficulty because of the abnormally high concentration of ferric ion which interferes with the precipitation of phosphorus, due probably to the formation of complexes of ferric ion and phosphate. Since it is possible to tie up ferric ion so completely, by the addition of phosphate to a solution, that many of the usual reagents will no longer precipitate iron, it would seem that when dealing with the reverse condition, a very small amount of phosphate in the presence of an excessive amount of iron, as is the case in a solution made by dissolving an iron or steel, the concentration of phosphate ion must be exceedingly low. N. E. Johann (Dissertation, Columbia University, 1921) found that the precipitation of phosphorus in steel was not complete in cold solution with the ammonium molybdate reagent but that it was necessary to heat the mixture to 60° C. With the cesium molybdate reagent it was found that precipitation of phosphorus was complete in cold solution even in the presence of this high concentration of ferric ion. Precipitation in cold solution is desirable for it should prevent to a large extent any tendency for molybdic acid to separate and should offer a favorable condition for the formation of a precipitate of constant composition.

Since many steels contain arsenic, though usually in amounts that do not effect their properties, it is necessary for the exact determination of phosphorus to remove arsenic before precipitating the cesium phosphomolybdate.

Method of procedure.

A sample of two grams of iron or steel was dissolved in 60 cc of nitric acid, specific gravity 1.135. The solution was taken to dryness three times in the presence of hydrochloric acid to decompose nitric acid. The residue was taken up with 20 cc of concentrated hydrochloric acid, 0.5 gram of iron in the form of ferrous chloride, free from phosphorus and arsenic, was added

and the solution boiled down to a volume of approximately 10 cc. An additional quantity of 10 cc of concentrated hydrochloric acid was added and the operation repeated three times to insure complete removal of arsenic by distillation as the chloride. Nitric acid was added to oxidize any ferrous chloride remaining and sufficient water to bring the solution to a volume of approximately 70 cc. The solution was rendered nearly neutral by the addition of sodium hydroxide, water added to make the volume 100 cc and to the cold solution were added rapidly 45 cc of the precipitating reagent. The solution was allowed to stand from twelve to eighteen hours and the determination of phosphorus completed in the manner previously outlined.

A test of the method on samples of iron and steel obtained from the Bureau of Standards gave results as follows:

Sample No. 11a

Cesium Method		Results Reported on Bureau of Standards Certificate		
	.009 % P.	.008 % P.	.006	.008
	.009	.008	.008	.008
	.009	.010	.007	.008
	.009	.008	.008	.012
	.009			
	.009		Average	.0082
	.008			
Average	.0088			

Sample No. 20a

Cesium Method		Results Reported on Bureau of Standards Certificate		
	.047 % P.	.043 % P.	.050	.045
	.046	.046	.047	.046
	.046	.046	.046	.047
	.045	.047	.044	.045
Average	.046			.048
			Average	.046

Sample No. 19b

Cesium Method		Results Reported on Bureau of Standards Certificate		
	.045 % P.	.044 % P.	.045	.044
	.044	.043	.043	.043
	.045	.045	.043	.042
	.044	.046	.043	.043
Average	.0445	.042	.042	
			Average	.043

An examination of these results shows that while those obtained by the cesium method are in general in fairly close agreement with the average values of the Bureau of Standards, they are in much closer agreement among themselves than are the latter. Since the Bureau of Standards have taken the most elaborate precautions to secure uniformity in the samples, it is but fair to assume that the deviations in the results are due wholly to experimental errors in the methods of analysis used.

SUMMARY

1. A review of the literature on the method for the precipitation of phosphorus as ammonium phosphomolybdate has been made, which indicates (1) a wide variation regarding the conditions for precipitation, (2) a wide variation in the method of washing the precipitate, (3) a wide variation regarding the treatment of the precipitate because of the presence of ammonia in the molecule, (4) uncertainty regarding the composition of the precipitate, (5) a wide variation in the factor used.

2. A new reagent for the precipitation of phosphorus has been prepared. This reagent is sensitive to low concentrations of phosphate ion, admitting of precipitation in cold solution and thus offering a favorable condition for formation of a precipitate of constant composition.

3. It has been shown that results obtained by this method have a considerably higher precision than those obtained by the ammonium phosphomolybdate method.

4. The applicability of this method of precipitation for the determination of phosphorus by the acidimetric method has been shown for pure phosphates and for iron and steel. In the latter case the reagent is sufficiently sensitive to low concentrations of prosphate ion that precipitation of phosphorus from an iron-phosphate complex is complete in cold solution.

5. The ratio between phosphorus and sodium hydroxide when phosphorus has been precipitated by this reagent has been found to be 1 to 22.7.

6. The action of the reagent with arsenate ion has been shown and a method demonstrated for the determination of phosphorus without interference of arsenic.

VITA

Grover C. Chandlee was born in Delta, Pa., September 5, 1884. He received the degree of Ph.B. from Franklin and Marshall College in June, 1907. In September, 1907, he was appointed an instructor in chemistry at the Pennsylvania State College. He received the degree of M.S. from that institution in June, 1913. During part of 1918-1919 he served as First Lieutenant in the United States Army, American Expeditionary Force. In 1921-1922, 1922-1923, and during the summers of 1922 and 1923 he was a graduate student in chemistry at Columbia University. In 1922 he received the degree of M.A. At present he is Professor of Chemistry at The Pennsylvania State College.

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